

Growth and characterization of ultrathin nitrided silicon oxide films

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This paper reviews recent progress in understanding microstructural and growth-mechanistic aspects of ultrathin (<4 nm) oxynitride films for gate dielectric applications. Different techniques for characterizing these films are summarized. We discuss several nitridation methods, including thermal (oxy)nitridation in NO, N₂O, and N₂ as well as a variety of deposition methods. We show that a basic understanding of the gas-phase and thin-film oxygen and nitrogen incorporation chemistries facilitates the processing of layered oxynitride nanostructures with desirable electrical properties.

1. Introduction

While “pure” SiO₂ films remained the principal material for gate dielectrics in MIS-based structures for more than three decades, the use of the traditional SiO₂ gate dielectric has become questionable for sub-0.25-μm ULSI devices [1–5]. Increasing problems with dopant (boron) penetration through ultrathin SiO₂ layers and direct tunneling for ultrathin (<2 nm) oxide films dictate the search for and aggressive exploration of new materials for future gate dielectric applications with better diffusion barrier properties and higher dielectric constants [6, 7]. At

this time, ultrathin silicon oxynitrides (SiO_xN_y or, more accurately, nitrogen-doped SiO₂) are the leading candidates to replace pure SiO₂ [8–24]. Oxynitrides exhibit several properties superior to those of conventional thermal O₂ oxides (SiO₂), the more important being suppression of boron penetration from the poly-Si gate and enhanced reliability. Nitrogen also reduces hot-electron-induced degradation [25]. The dielectric constant of the oxynitride increases linearly with the percentage of nitrogen from $\epsilon(\text{SiO}_2) = 3.8$ to $\epsilon(\text{Si}_3\text{N}_4) = 7.8$ [26, 27], though one should note that most SiO_xN_y films grown currently by thermal methods are lightly “doped” with N (<10 at.%) and therefore have a dielectric constant only slightly higher than that of pure SiO₂.

Recent publications suggest that the performance of CMOS-based devices depends on both the concentration and distribution of the nitrogen atoms incorporated into the gate dielectric [14, 16, 18, 28–30]. For example, excessive nitrogen at the interface may reduce peak carrier mobility in the channel of MOSFETs and may allow boron accumulation in the oxide, which, in turn, may result in device instabilities [28]. The optimal nitrogen profile is determined by its specific application, although our incomplete understanding of the atomic-scale structural and electronic properties of dielectrics makes the desired structure an imperfectly defined goal. One possibility is an SiO_xN_y film with two nitrogen-enhanced layers: first,

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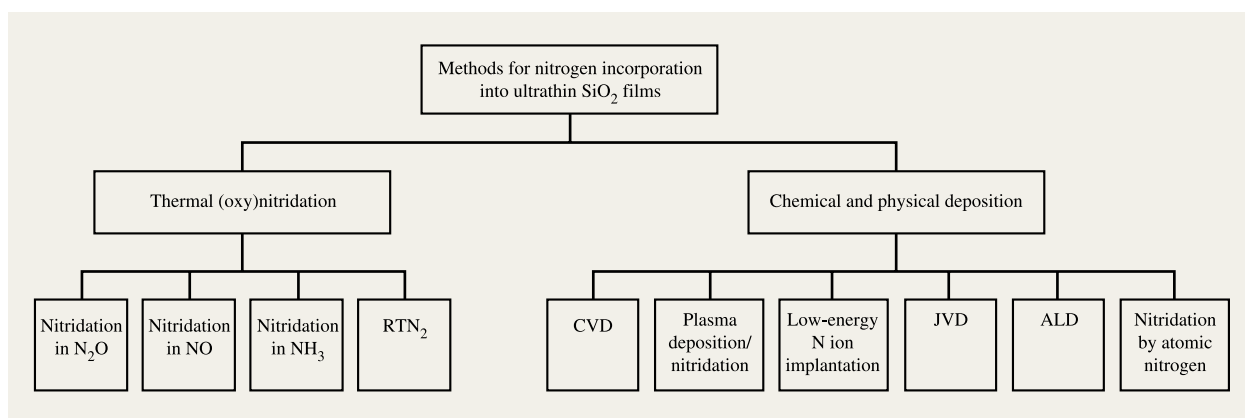


Figure 1

Different nitridation methods.

nitrogen at or near the Si/SiO₂ interface to improve hot-electron immunity, and second, an even higher nitrogen concentration at the SiO₂/polysilicon interface, as this is where it can best be used to minimize the penetration of boron from the heavily doped gate electrode [29]. The boron flux can be quite large (depending upon the thermal budget) and, therefore, higher nitrogen concentrations at the poly-Si interface are needed [28]. Although the actual “ideal” amounts of nitrogen required at each interface are not known, typical interfacial contents are of the order of $(0.5\text{--}1) \times 10^{15} \text{ cm}^{-2}$ near each interface. The best methods to produce the desired ultrathin SiO_xN_y films are still under debate.

Nitrogen may be incorporated into SiO₂ using either thermal oxidation/annealing [8, 9, 12–14, 31–39] or chemical and physical deposition [15, 16, 18, 19, 40, 41] methods (**Figure 1**). Thermal nitridation of SiO₂ in NO or N₂O generally results in a relatively low concentration of nitrogen in the films, of the order of 10^{15} N/cm^2 [20, 29, 33, 42]. Since nitrogen content increases with temperature, thermal oxynitridation is typically performed at high temperatures, i.e., $>800^\circ\text{C}$ [20, 29, 33, 42]. For more heavily N-doped SiO_xN_y films, other deposition methods, such as chemical vapor deposition (CVD) [40] with different precursors and its low-pressure (LP) and/or rapid thermal (RT) variants [18], jet vapor deposition (JVD) [43], atomic layer deposition (ALD) [44], or nitridation by energetic nitrogen particles (plasma, N atoms, or ions) [45–55], can be used. These nitridation methods can be performed at lower temperatures, $\sim 300\text{--}400^\circ\text{C}$. However, low-temperature deposition methods may result in nonequilibrium films, and subsequent thermal processing steps are often required to improve film quality and minimize defects and induced damage [19, 56]. Because

the thermodynamics [57, 58] of the SiO_xN_y system and the kinetics [12, 20, 29, 32, 38, 59–63] of nitrogen incorporation are rather complex, these different methods produce oxynitride films with different total nitrogen concentrations and depth distributions. From a scientific viewpoint, the addition of N into the Si–O system opens a number of questions concerning microstructure, defects, and growth mechanisms, issues which are still under intense debate even for the much simpler “pure” SiO₂/Si system [64–71].

Characterizing the nitrogen distribution in ultrathin films with the required sub-nm accuracy is an analytical challenge. Conventional depth profiling approaches, such as SIMS (secondary ion mass spectroscopy) [9, 14, 18, 34, 72] and HF etch-back methods [12, 33, 35] [in combination with XPS (X-ray photoelectron spectroscopy), NRA (nuclear reaction analysis), etc.], offer limited depth resolution, especially for ultrathin dielectrics. In addition, SIMS analysis is complicated by matrix effects [73], while HF etching may introduce nonuniform oxide removal (especially in the presence of local nitrogen-rich regions) and other deleterious chemical effects. We have recently demonstrated [62, 63, 74–76] that high-resolution ($\Delta E/E \approx 0.1\%$) medium-energy ion scattering (MEIS) [77] is a useful technique for accurately obtaining the depth distribution profile of nitrogen in 1–4-nm oxynitride films with sub-nm accuracy.

In this paper, we review our recent progress in 1) characterizing nitrogen depth profiles (by MEIS [42, 74, 76]) and bonding (by XPS [78]) of ultrathin SiO_xN_y films, and 2) understanding the mechanisms of nitrogen incorporation into ultrathin oxide films [42, 62, 63, 79, 80]. We demonstrate how this basic knowledge can be used to guide nitrogen nanoengineering technology, in particular to

produce layered nitrogen structures [81]. A significant part of the paper is devoted to thermal oxynitridation of Si in NO and N₂O. Other nitridation methods are also briefly discussed.

2. Thermodynamics of the Si–N–O system

The bulk phase diagram of the Si–N–O system is shown in **Figure 2**. The diagram consists of four phases: Si, SiO₂ (cristobolite, tridymite), Si₃N₄, and Si₂N₂O [57, 58]. The three compound phases have similar structural units: SiO₄ tetrahedra for SiO₂, Si₃N₄ tetrahedra for Si₃N₄, and slightly distorted SiN₃O tetrahedra for Si₂N₂O, implying that the phases can be converted from SiO₂ to Si₂N₂O and finally to Si₃N₄ by replacing oxygen with nitrogen. However, the nitride (Si₃N₄) and the oxide (SiO₂) phases never coexist in the bulk under equilibrium conditions. They are always separated by the oxynitride (Si₂N₂O), which is the only thermodynamically stable and crystalline form of silicon oxynitride.

A puzzling question is why nitrogen atoms are incorporated at all in SiO₂. According to thermodynamic equilibrium, nitrogen should not incorporate into an SiO₂ film that is grown on Si in almost any partial pressure of oxygen, i.e., $>10^{-17}$ atm, depending upon temperature [57, 58]. One can see from Figure 2 that the Si₂N₂O/SiO₂ phase boundary exists at about 10^{-18} atm for $T = 1400$ K. At any oxygen partial pressure greater than that, which surely exists in a furnace or rapid thermal processing (RTP) reactor or, for example, during N₂O or NO decomposition at high temperatures, only SiO₂ phases (crystalline or amorphous) should form. Therefore, nitrogen in bulk SiO₂ is not thermodynamically stable.

At least two reasons for the presence of nitrogen in the SiO₂ film can be suggested. First, nitrogen atoms may simply be kinetically trapped at the reaction zone near the interface (i.e., the nitrogen is present in a nonequilibrium state, where the rate of the transition to equilibrium is slow and some N is trapped) or by structural defects in the SiO₂ film [82]. The basic idea in this model is that nitrogen brought into the film during oxynitridation (as, for example, NO; see below) reacts only with Si–Si bonds at or near the interface, not with Si–O bonds in the bulk of the SiO₂ overlayer. Alternatively, the nitrogen at the interface may indeed be thermodynamically stable due to the presence of free-energy terms that are not yet understood. For example, nitrogen may lower the interfacial strain known to exist at the SiO₂/Si interface. This could explain why incorporated nitrogen (especially in N₂O or NO oxides) is often associated with the Si/SiO₂ interface, consistent with a special, stabilizing role of the nitrogen at the interface. Even when nitrogen is implanted into Si, it tends to migrate to the Si/SiO₂ interface during oxidation and be incorporated in the SiO₂ [83, 84]. Therefore, there is some evidence that the nitrogen

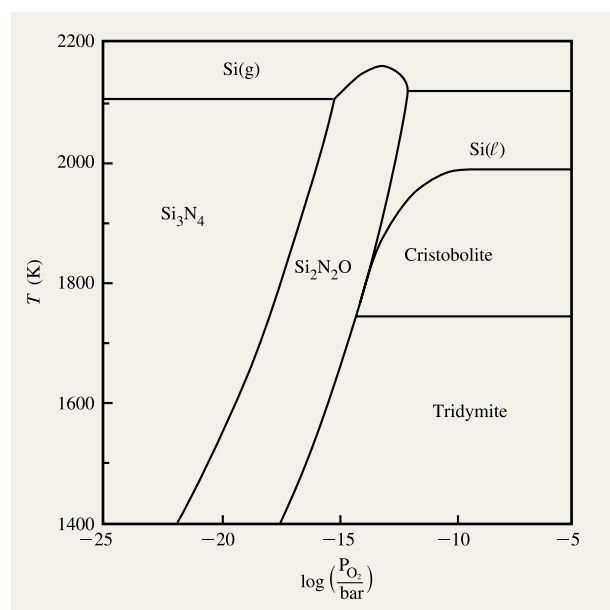


Figure 2

Thermodynamic phase diagram of the Si–N–O system (after [29, 58], with permission).

plays a specific role at the interface, but also that it is not stable away from it. On the other hand, nonequilibrium techniques (for example, plasma nitridation) have yielded oxynitrides with much higher concentrations of incorporated nitrogen (including top-surface nitridation [49]) than thermal oxynitridation methods (e.g., in NO, N₂O, N₂). This fact seems to be supportive of the “kinetic trapping” concept. Finally, we note that the favorable thermodynamics of the SiO₂ phase discussed above may be the reason why Si₃N₄ films (produced by JVD or other methods) always contain some oxygen; of course, contamination by H₂O, O₂, etc. with a high sticking coefficient would also result in mixed oxide–nitride phases.

3. Diffusion-barrier properties of nitrided layers

An important property of nitrogen in nitrided oxides is that it forms a barrier against the diffusion of boron. Concurrent with this, it also lowers the diffusion rates for oxygen, nitric oxide, and other dopants, significantly slowing the rate of further oxidation or nitridation [21, 32, 34, 63, 82, 85–90]. For example, for a 2-nm oxynitride with ~ 1 ML (monolayer) of nitrogen (6.8×10^{14} N/cm²) located near the interface, the rate of continued oxidation at 900°C decreases by at least a factor of 4 relative to the pure oxide. A reasonable argument can be made that the decrease in film growth rate (due to nitrogen) results from

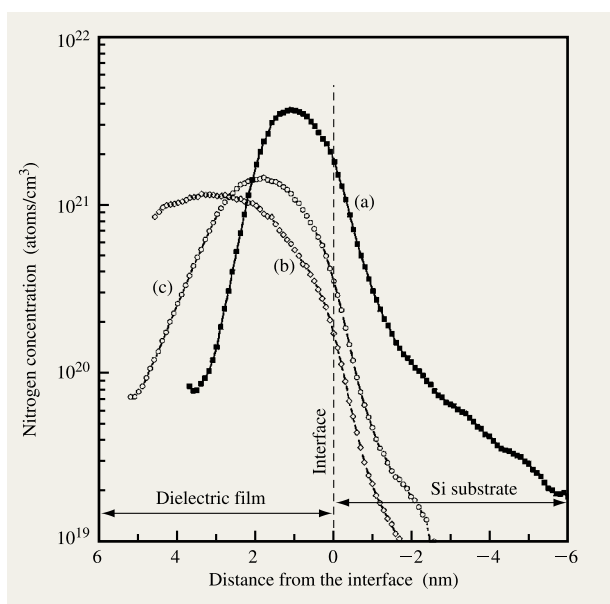


Figure 3

Nitrogen depth profiles obtained by SIMS (Evans East) for (a) 4.5-nm SiO_2 film annealed in NO at 950°C for one hour; (b) film grown in N_2O in a furnace at 850°C for 110 min; and (c) oxynitride film grown by RTP in N_2O at 1000°C for 2.3 min (after [74], with permission).

a decreased rate of diffusion. The density of nitrides and oxynitrides is higher than that of the pure oxide [40]; thus, the diffusivity of NO, O_2 , N_2 , or other nonreactive molecular species such as noble gases should be lower in the nitrogen-containing films. However, another property involving N bonds may be equally important: The lattice itself may become more rigid on an atomic level. The three bonds connected to each nitrogen (as in Si_3N_4) are more constrained than the two bonds of each O atom in SiO_2 , where the Si–O–Si bond angles can go from 120° to 180° with little change in energy; this may also contribute to a decrease in the ability of the nitrated lattice to permit diffusion of atoms and small molecules. The latter argument is valid for either an interstitial diffusion mode (of molecules), or an exchange-hopping substitutional mode (of excess atoms).

By analogy, both physical (e.g., density) and chemical arguments have been used to explain the important effect of the reduced penetration rate of boron from the poly-Si gate into nitrated oxides. (Boron penetration causes threshold voltage shifts and degrades reliability.) To explain the “stopping power” of the nitrogen in oxides, a model assuming boron diffusion via peroxy linkage defects (Si–O–O–Si bonds), whose concentration changes under different processing conditions and film thicknesses, has

been suggested [91]. For a 1.5-nm SiO_2 film, the diffusivity at 900°C would increase by a factor of 24 as compared with 10-nm oxides. According to this model, the role of nitrogen is that the N atoms compete with B for occupation of the defect sites. The model was criticized by Ellis and Buhrman [92], who argued that 1) Si–O–N–O–Si structures, which should form after N passivation, are not observed in XPS; and 2) according to percolation theory, to fit the experimental data the peroxy defects should have an unreasonably high concentration (~40% of the Si–O–Si bonds). Ellis and Buhrman developed a model in which boron diffuses substitutionally for Si atoms, and the role of the Si–N bond is to impede substitution for that Si atom [92]. The model was incorporated into a Monte Carlo simulation and showed good agreement with experimental data.

Another interesting aspect of the diffusion barrier property of nitrated layers is that silicon interstitials generated during the film growth reaction at the interface are blocked from diffusing into the oxide [93]. This results in an enhanced flux of the interstitials into the Si substrate, which in turn yields an increased density of oxidation stacking faults and may also affect oxidation-induced diffusion [93]. Finally, we note that other chemistries may play an important role both in film growth processes and in the more technically important issue, electrical defects that occur in the final devices. Hydrogen, water, and various other species quite possibly exist at finite concentrations [94]. For example, both fluorine and hydrogen enhance the boron diffusion rate [91]. Hydrogen may also play an important role in the diffusion/reaction processes during (oxy)nitride formation [40].

4. Materials characterization of ultrathin nitrated oxides

Two major problems in measuring nitrogen in SiO_xN_y films are the following: 1) In many cases the concentration of nitrogen in the film is rather low (as an example, in earlier studies of NO oxynitrides [95] it was claimed that the films are essentially SiO_2 because the nitrogen was undetectable at that time); and 2) the films in question are very thin (<5 nm), suggesting that sub-nm depth resolution is required to monitor nitrogen depth profiles. Over the past few years, several techniques, such as secondary ion mass spectroscopy (SIMS) [18, 34, 72, 73, 78], nuclear reaction analysis (NRA) [29, 32, 33, 38, 59, 80, 96, 97], medium-energy ion scattering (MEIS) [39, 42, 62, 63, 74–76, 80], X-ray photoelectron spectroscopy (XPS) [12, 30, 34, 35, 37, 48, 74, 78, 87, 98–101], Auger electron spectroscopy (AES) [19], Fourier transform infrared spectroscopy (FTIR) [102], spectroscopic ellipsometry [103], and others have been utilized to study nitrogen concentrations, depth profiles, nitrogen bonding, and microstructure of

Table 1 Selected nuclear reactions for oxynitride characterization.

Target element	Nuclear reaction	Energy (keV)	Sensitivity (atoms/cm ²)
H	H(¹⁵ N, αγ) ¹² C	6420	~10 ¹⁴
D	D(³ He, p) ⁴ He	700	~10 ¹²
¹⁴ N	¹⁴ N(d, α _{0,1}) ¹² C	1100	~5 × 10 ¹³
¹⁵ N	¹⁵ N(p, α) ¹² C	1000	~10 ¹²
¹⁵ N	¹⁵ N(p, αγ) ¹² C	429	~10 ¹³ (estimated)
¹⁶ O	¹⁶ O(d, p) ¹⁷ O	850	~10 ¹⁴
¹⁸ O	¹⁸ O(p, α) ¹⁵ N	730	~10 ¹²
¹⁸ O	¹⁸ O(p, α) ¹⁵ N	151	~10 ¹³ (estimated)
²⁸ Si	²⁸ Si(p, γ) ²⁹ P	371	
²⁹ Si	²⁹ Si(p, γ) ³⁰ P	324	~10 ¹³
		417	(estimated)
³⁰ Si	³⁰ Si(p, γ) ³¹ P	499	~10 ¹³ (estimated)

oxynitrided films. Below we outline the features and the utility of these techniques for ultrathin oxynitride studies.

SIMS, a standard technique used in the industry to monitor concentration profiles in semiconductor structures, was one of the first methods applied to the nitrogen depth distribution problem in oxynitrided films. The technique has a rather high sensitivity (of the order of 0.001 at.%), can be performed rapidly, and shows good long-term reproducibility [73]. As an example, **Figure 3** illustrates nitrogen depth profiles for ~5-nm oxynitride films grown by thermal oxynitridation of Si(100) in N₂O (both in a furnace and in an RTP reactor), and in O₂ followed by NO [74]. One can see different depth profiles depending on the processing conditions. The NO-annealed film has the highest concentration of nitrogen incorporated near the SiO_xN_y/Si interface. The RTN₂O (rapid thermal oxynitridation) film also shows nitrogen located near the interface, whereas the furnace-grown film has a broader nitrogen depth distribution. Both N₂O oxynitrides have nitrogen concentrations lower than the NO-annealed film. The technique begins to reach the limits of depth resolution (estimated to be ~2–3 nm) for sub-5-nm films. Another more important complication for SIMS analysis are “matrix effects,” in which the sputtered nitrogen ion yield depends strongly on the local film chemistry around the nitrogen. For example, the (CsN⁺) ion yield from nitrogen in bulk Si is about six times smaller than in SiO₂, while that for N near the interface is about three times that observed in the bulk of the SiO₂ film [73]. The use of CsN⁺ ions as the detected species

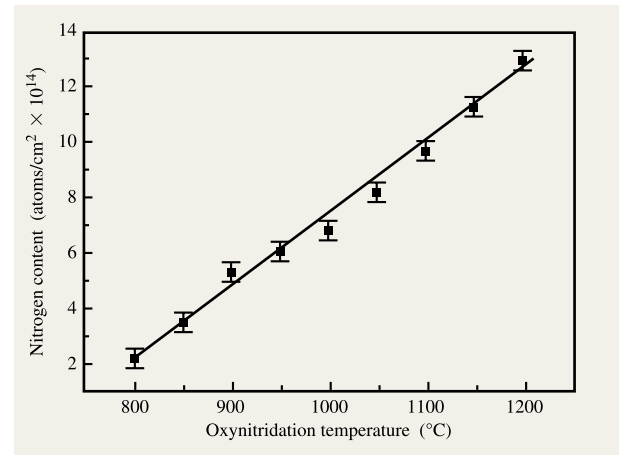


Figure 4

Nitrogen content in 10-nm oxynitride films grown in N₂O by RTP, as measured by NRA (after [33]).

seems to minimize the matrix effect, since for negative ions matrix effects are even more severe. In most cases, SIMS analysis is also complicated by surface contamination and initial sputtering effects which make measurements of the nitrogen in the top (~1 nm) surface layers not very meaningful. Finally, one more metrological aspect of the SIMS analysis is that the N concentration shown for the interface peak (see Figure 3) may not be accurate due to ion mixing. The areal density of the N peak should be used instead. Reference samples (especially with different nitrogen distributions) calibrated by other quantitative methods (NRA, MEIS, etc.) may be helpful for more accurate quantitative SIMS analysis.

NRA analysis of oxynitrides is based on the detection of protons, α-particles, and γ-rays generated in nuclear reactions of nitrogen, oxygen, silicon, and hydrogen (deuterium) induced by high-energy charged particles (**Table 1**) [29, 32, 33, 38, 59, 80, 96, 97]. The cross sections for these reactions can be determined in independent calibration experiments, and the signal-to-background ratio is in many cases quite favorable. Since the nuclear reaction rates are sensitive only to the number of nuclei in the films, the technique yields absolute concentrations of the species investigated. In particular, the technique allows one to determine the absolute concentration of ¹⁴N with an accuracy of ~7–10% and a detection limit of ~5 × 10¹³ atoms/cm² via the reaction of ¹⁴N(d, α_{0,1})¹²C induced by 1.1-MeV deuterons. **Figure 4** shows the nitrogen content (which is an increasing function of temperature) in oxynitride films grown by rapid thermal oxynitridation in N₂O [33]. The oxygen content in the films can also be measured by NRA, for example by the ¹⁶O(d, p)¹⁷O

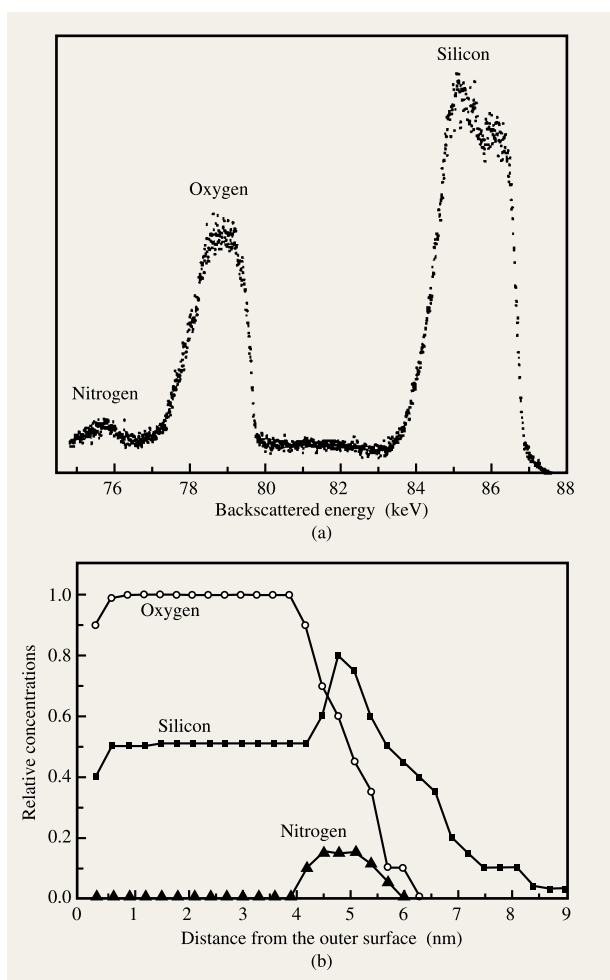


Figure 5

(a) MEIS spectrum for a 4.5-nm SiO_2 film annealed in NO at 950°C for one hour. Primary energy of the proton beam is 97.2 keV. The spectrum is taken in a channeling direction. Scattering angle is 125° . Corresponding oxygen, silicon, and nitrogen depth profiles are shown in part (b).

reaction at 850 keV. This allows one to calculate the thickness of the films (provided that film density is known). An additional advantage of the NRA technique is the detection of nitrogen (^{15}N) and oxygen (^{18}O) isotopes with the help of the following reactions: $^{15}\text{N}(\text{p}, \alpha)^{12}\text{C}$ at 1000 keV, $^{18}\text{O}(\text{p}, \alpha)^{15}\text{N}$ at 730 keV, and the resonant reactions of $^{15}\text{N}(\text{p}, \alpha\gamma)^{12}\text{C}$ at 429 keV and $^{18}\text{O}(\text{p}, \alpha)^{15}\text{N}$ at 151 keV. Isotopic labeling has been proven to be a useful method to study mechanistic aspects (including nitrogen and oxygen transport) of silicon (oxy)nitridation [38, 59, 97, 104]. Owing to the narrow resonances (with widths of 120 and 100 eV, respectively), the latter two reactions can be used for depth profiling of ^{15}N and ^{18}O on an

approximately 1-nm scale under favorable conditions. Depth profiling can also be performed by an HF acid etch-back with subsequent NRA measurement of N remaining in the film [13]. One more useful application of NRA is based on its ability to measure hydrogen/deuterium [$\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ at 429 keV and $\text{D}(^3\text{He}, \text{p})^4\text{He}$ at 700 keV] since H/D is believed to be important in both the nitridation mechanism and device performance [105, 106]. Finally, we note that nitrogen, oxygen, silicon, and hydrogen can also be monitored by the technique of elastic recoil detection (ERD) of primary MeV ions [86].

MEIS, another ion beam technique, is based on the same principles of ion-solid interactions as is conventional Rutherford backscattering spectroscopy (RBS) [77]. Because of the lower ion energy used in MEIS (typically 100 keV, at which the energy loss of protons in a solid is maximal), and the use of a high-resolution toroidal electrostatic ion energy analyzer [107] ($\Delta E/E \approx 0.1\%$), almost-monolayer depth resolution can be obtained [108, 109]. We have demonstrated that a 0.3–0.5-nm accuracy (near the top surface or for very thin films) in the nitrogen depth profiles can be achieved [42, 74]. To our knowledge, this is the best depth resolution for nitrogen in SiO_xN_y films achieved so far. However, due to the statistical nature of the ion energy loss in the solid (straggling effect) [110], the resolution decreases with increasing distance from the surface. MEIS allows one to monitor simultaneously both absolute concentrations and depth profiles of N, O, and Si in the film. The detection limit of nitrogen in SiO_2 is about $2\text{--}3 \times 10^{14}$ atoms/ cm^2 , depending on the film thickness and the width of the nitrogen distribution in the film. It is worth noting that, in opposition to other depth-profiling techniques (e.g., SIMS), both the sensitivity to nitrogen and the depth resolution increase with decreasing dielectric film thickness. Another strength of MEIS is mass sensitivity, which enables isotopic (^{18}O and ^{16}O) labeling experiments [111, 112]. Light elements (for example, hydrogen and boron) can also be detected in the elastic recoil configuration, as demonstrated by Copel and Tromp [113, 114].

Figure 5(a) shows a typical MEIS spectrum for an SiO_2 film annealed in NO. Three peaks are seen in this spectrum, corresponding to nitrogen, oxygen, and silicon. The lighter mass (nitrogen) yields a peak at lower energy, as given by classical two-body scattering kinematics [77]. The areas under the peaks (after corrections for the known cross sections) are proportional to the total amounts of oxygen and nitrogen in the film [77]. Obviously, the amount of nitrogen is much smaller than that of oxygen. The shape of the nitrogen peak is determined by the depth distribution of nitrogen in the film. Because of energy loss arising from electronic

excitations, protons backscattered from nitrogen atoms closer to the Si-SiO_xN_y interface have lower energy than those scattered off the atoms near the surface. Accurate depth distributions [Figure 5(b)] of Si, O, and N are deduced from simulations of energy spectra, as discussed in [111]. More details about the MEIS setup, data acquisition and analysis, and the isotopic labeling technique can be found elsewhere [74, 108, 111, 112, 115–117].

The above ion beam methods are unfortunately not capable of examining local nitrogen bonding in (oxy)nitrided films. Photoemission (XPS) is a common technique used to help determine local bonding configurations of atoms on a surface or in a thin film [68, 118–121]. XPS analysis is based on the fact that the energies of the electronic core levels are altered by the local electronic configurations. The observed energy levels shift with changing local chemical environment (the so-called chemical shifts). Early XPS studies were limited to the detection of nitrogen at the interface of SiO₂ annealed in nitrogen [87, 98]. More recent high-resolution (including synchrotron-based) photoemission studies of core levels of nitrogen (N 1s) and silicon (Si 2p) atoms were useful in understanding nitrogen bonding and depth distribution (with HF etch-back or variable photoelectron takeoff angle methods) [35, 37, 78, 99, 122]. Depth analysis in XPS is determined by the escape depth of the N 1s or Si 2p photoelectrons, which are of the order of 2–3.5 nm for conventional AlK_α or MgK_α X-ray sources. N 1s spectra for NO and N₂O oxynitrides are shown in Figure 6 [78]. The nitrogen spectrum for the N₂O-grown film has much lower intensity than that of the NO oxynitride, which indicates that an NO source is more effective in terms of nitrogen incorporation into the dielectric film. A second feature to point out is that the spectra for both NO and N₂O oxynitrides have similar shapes (see inset), suggesting that the local bonding configurations of nitrogen in the two films are similar.

A more detailed analysis of the N 1s peak shape shows that the peak is asymmetric and consists of at least two components [35, 78, 99]. The lower binding energy (BE) component at ~397.6 eV (calibrated with respect to the Si 2p peak at 99.2 eV) is located closer to the interface, while the higher BE component at 398.3–399.0 eV (the thicker the film, the higher the value) corresponds to nitrogen atoms located further into the overlayer film. The lower BE peak can be assigned to N atoms bonded to three Si atoms, as follows from the observation of an N 1s peak at ~397.6 eV from a reference Si₃N₄ film [35, 99]. The shift of the higher BE component originates from both electrostatic (charging, core hole screening) and structural effects. The structural effects may include different bond length and bond angles in the “bulk” of the film and near the interface, strain near the interface,

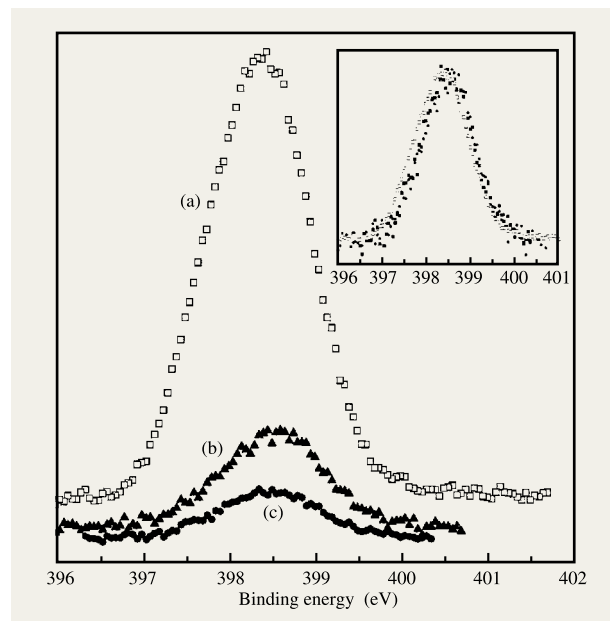


Figure 6

N 1s XPS spectra for (a) ~2.5-nm oxynitride film grown in NO at 1000°C; (b) ~6-nm (as grown at 1000°C) RTN₂O film; and (c) the same film HF-etched back to ~3 nm. The inset shows the same spectra normalized to the same maximum intensity (after [78]).

and/or second-neighbor effects (i.e., bonding/atoms in the shell of second neighbors near the interface may be different from those in the middle of the oxynitride film) [100]. N–O bonds are unlikely to be present at high concentration in the NO and N₂O oxynitrides because the chemical shift of ~1.5 eV (relative to the N–Si bond) calculated recently [100] for this configuration is larger than any experimentally observed ones. Recent work by R. Opila and J. Chang demonstrated that nitrogen profiles obtained from angular resolved XPS were consistent with MEIS depth profiles. They also showed that for oxynitride films processed by plasma, metastable nitrogen states may be observed with binding energies greater than 400 eV. Finally, we note that XPS is also useful in obtaining film thickness [123] (from the ratio of Si 2p peaks corresponding to the film and Si substrate) and interface structure [30, 35, 68, 118, 121, 124] (from the concentration of Si¹⁺, Si²⁺, and Si³⁺ suboxide states observed in the Si 2p spectrum). Recent XPS studies of the suboxide states in N₂O oxynitrides were interpreted as giving evidence for a lower defect density at the SiO_xN_y/Si interface with respect to the SiO₂/Si interface [35]. However, an opposite effect (i.e., an increased concentration of the Si¹⁺ state and an unchanged concentration of the Si¹⁺ and Si²⁺) has also been reported

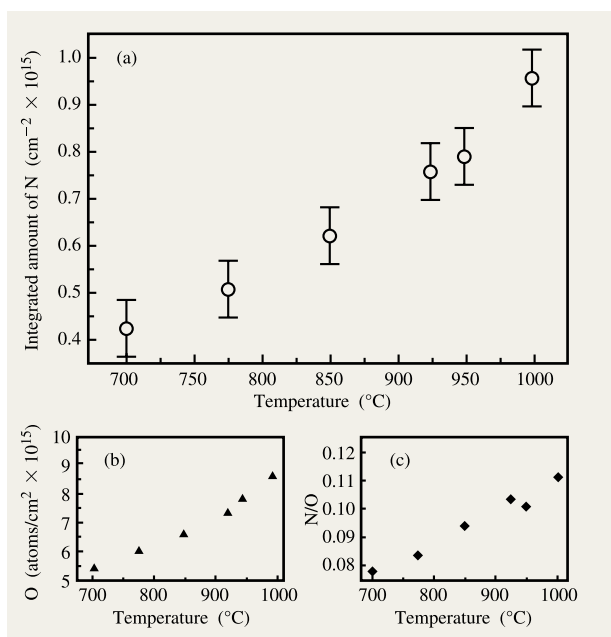


Figure 7

Concentrations of (a) nitrogen and (b) oxygen, and (c) nitrogen-to-oxygen ratio in ultrathin SiO_xN_y films grown in NO, as measured by MEIS (after [42], with permission).

[30]. Another electron spectroscopy, AES, can also be used to measure nitrogen content in SiO_xN_y films and has been used effectively in studies of plasma-nitrided samples [19]. Though the AES sensitivity to nitrogen is similar to that of XPS, the interpretation of spectral features is usually more difficult than in XPS because the Auger electron emission process is more complex than photoemission.

Finally we discuss some other techniques for characterizing nitrogen and SiO_xN_y film microstructure. The amount of nitrogen can be crudely estimated from oxidation kinetics measurements. Since nitrogen significantly retards transport/reactions in (oxy)nitrided films [32, 34], this simple method can be used to monitor the presence of nitrogen in the film and to compare its relative value in different samples. However, the retardation rate depends not only on the N concentration but also on the depth distribution. A given amount of N evenly distributed in the film would produce a diffusion barrier quite different from one in which the nitrogen distribution is sharply peaked, making quantitative analysis difficult. Spectroscopic (immersion) ellipsometry results on N_2O - and NO-grown oxynitrides show an agreement with SIMS measurements, though one should keep in mind that ellipsometric analysis is very dependent on parameters

and models [103]. A structural two-layer model of N_2O oxynitride films with an ~ 1.4 – 1.6 -nm-thick $\text{Si}_2\text{N}_2\text{O}$ phase near the interface was suggested to explain a shift of the main peak in the FTIR spectrum as a function of the thickness of the films [102]. Optical second-harmonic spectroscopy has been used to study strain at the interface [125, 126]. Roughness at the $\text{SiO}_x\text{N}_y/\text{Si}$ interface was studied by X-ray diffraction. It was found that, for N_2O oxynitrides, the (RMS) roughness is smaller than for pure SiO_2 films and decreases with temperature [33].

5. Thermal (oxy)nitridation methods

• Nitrogen incorporation into ultrathin dielectrics by NO processing

Oxidation of silicon and annealing of SiO_2 in nitrous (N_2O) or nitric (NO) oxides are the leading hydrogen-free processing methods for making nitrided oxides by conventional thermal routes [20, 21, 29]. Oxynitridation in N_2O is particularly attractive because 1) it allows one to incorporate what appears to be an appropriate amount of nitrogen near the $\text{SiO}_x\text{N}_y/\text{Si}$ interface (typically $\sim 5 \times 10^{14}$ atoms/cm²); and 2) its processing similarity to O_2 permits N_2O to replace oxygen in oxidation reactors/furnaces. However, among other factors, oxynitridation in N_2O is complicated by the fast gas-phase decomposition of the molecule into N_2 , O_2 , NO, and O at typical oxidation temperatures, 800–1100°C (see the subsection on gas-phase N_2O decomposition which follows). NO is now believed to be responsible for nitrogen incorporation into the film [21, 29, 31, 37, 60, 127, 128], suggesting that understanding oxynitridation in NO is a necessary step before considering more complex gases such as N_2O . If NO is the main species responsible for nitrogen incorporation into the film, oxynitridation in pure NO should be considered for ultrathin dielectrics, especially in processes in which thermal budget and film thickness issues are crucial. Compared to N_2O , oxynitridation in NO results in more nitrogen incorporation at equivalent temperatures [14, 34, 37, 74, 82]. In addition, NO oxynitrides exhibit lower leakage currents and interface defect densities, as well as improved electrical stress properties [14, 34]. However, channel mobility may be reduced if the nitrogen concentration near the interface is too high.

Figure 7 shows the total amounts of oxygen and nitrogen in ultrathin films on Si(100) after exposure in NO for an hour in the temperature range of 700–1000°C [42]. As the temperature increases, the total amounts of both nitrogen and oxygen increase. One should also note that the ratio of nitrogen to oxygen in the film increases with increasing temperature (increasing by $\sim 50\%$ from 700 to 1000°C). This was also observed during the initial stage of the interaction of NO with Si(111) at much lower pressure

(10^{-6} Torr) [129]. In other words, the film becomes more nitride-like at higher temperatures. The fact that the concentration of nitrogen increases with temperature has an important implication for the (oxy)nitridation of silicon in N_2O . It was observed that in the case of N_2O , a higher (oxy)nitridation temperature also gives rise to a higher nitrogen content in the film (Figure 4); this was attributed to a higher percentage of NO in the product stream resulting from the N_2O gas-phase decomposition at higher temperatures. Our results with NO as the only reactive gas clearly show that the solid-state chemistry is also important in the understanding of the incorporation and distribution of nitrogen in the dielectric layer.

Quantitative MEIS nitrogen depth profiles corresponding to NO oxynitrides grown at different temperatures are shown in **Figure 8** [42]. The width of the nitrogen-containing region increases with temperature. As the position of the interface (deduced from the oxygen depth profile and marked by arrows) propagates deeper into the Si substrate with increasing temperature, the nitrogen follows the movement of the interface such that, for the samples we examined, the nitrogen is distributed almost evenly in the films (also observed in a recent XPS/ Ar^+ sputtering depth profiling study [37]), except for the very near-surface SiO_2 region. These results are inconsistent with a model of a (continuous) single silicon nitride (Si_3N_4) layer near the interface. We further note that while recent SIMS results [34] on silicon (furnace) nitridation in NO were interpreted in terms of a nitrogen distribution sharply peaked on the substrate (silicon) side of the interface, rather than in the near-interfacial oxide, our MEIS studies did not find any evidence of significant nitrogen incorporation into the substrate. In addition, multiple features in angularly dependent core-level (N 1s and Si 2p) photoemission [34, 35, 74] and the multiphase nature of EPR signals from oxynitrides [130] suggest more complex (other than a single Si_3N_4 phase) local chemical bonding in the film.

Owing to the relatively high concentration of nitrogen incorporated into NO films, the kinetics of reoxynitridation are very slow. (The role of nitrogen in retarding the oxidation rate is discussed by us [32, 63] and by others [87, 88] elsewhere.) The thicknesses of the films after clean silicon surface exposure at 700–1000°C for one hour were only ~1.5–2.5 nm (Figure 8), consistent with earlier kinetic studies [95]. From a practical viewpoint, the slower growth of the oxynitride compared to a pure oxide facilitates good thickness control in the ultrathin regime during high-temperature processing. To make a thicker film, a thin preoxide (SiO_2) of desired thickness can first be formed, followed by an NO anneal. Typically NO-annealed preoxides yield nitrogen distributions different from the NO-grown films; that is, the nitrogen becomes concentrated near the interface [Figure 5(b)]. The kinetics

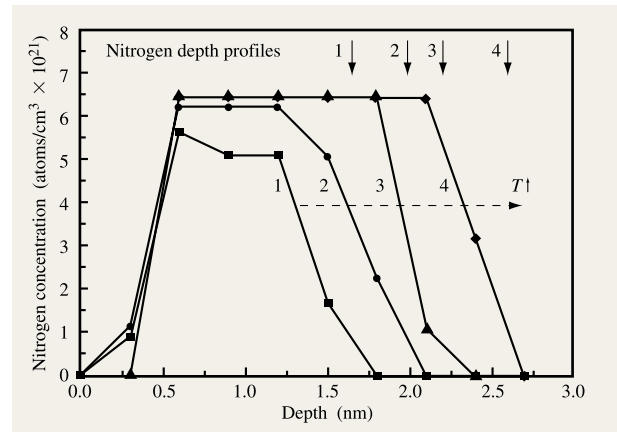


Figure 8

Nitrogen MEIS depth profiles (as a function of the distance from the outer surface) for oxynitride films grown in NO at 700°C (1), 850°C (2), 925°C (3), and 1000°C (4). The arrows show interface position for each film (after [42]).

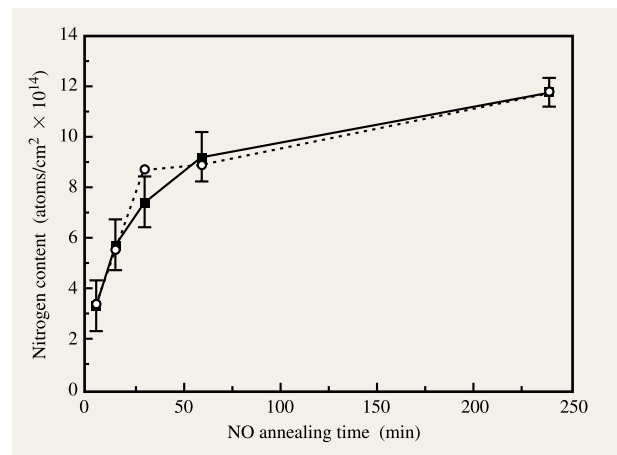


Figure 9

Kinetics of nitrogen accumulation in a 4.5-nm preoxide annealed in NO at 850°C. The solid symbols represent the data obtained by MEIS; open symbols show NRA results.

of nitrogen accumulation in a 4.5-nm SiO_2 film annealed in NO at 850°C is shown in **Figure 9**. One can see that after a fast initial accumulation, the rate of nitrogen incorporation becomes much slower at >60 min. Also noteworthy is that the total concentration of nitrogen for an NO-annealed preoxide is comparable to the concentration of an NO-grown film oxidized under equivalent conditions, at least for long oxynitridation times (cf. Figure 7).

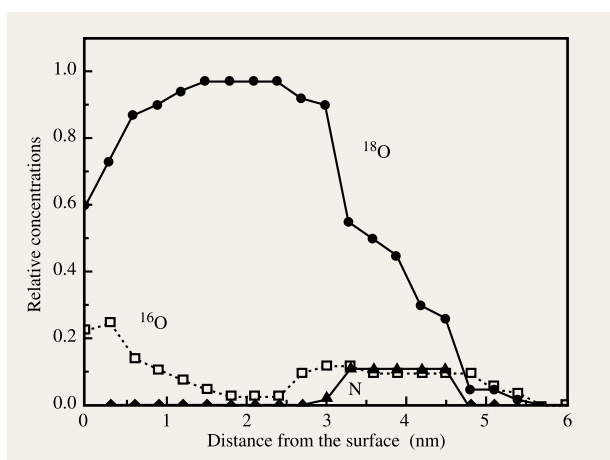


Figure 10

Isotopic labeling of the silicon oxynitridation in NO. The ¹⁸O (solid circles), ¹⁶O (open squares), and N (solid triangles) depth profiles are obtained for an Si¹⁸O₂ film annealed in N¹⁶O.

Table 2 Reaction scheme for N₂O decomposition.

1.	$\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}$
2.	$\text{N}_2\text{O} + \text{O} \rightarrow \text{NO} + \text{NO}$
3.	$\text{N}_2\text{O} + \text{O} \rightarrow \text{N}_2 + \text{O}_2$
4.	$\text{O} + \text{O} \rightarrow \text{O}_2$
5.	$\text{NO} + \text{O} \rightarrow \text{NO}_2$
6.	$\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$
7.	$\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{NO} + \text{O}_2$
8.	$\text{NO}_2 \rightarrow \text{NO} + \text{O}$
9.	$\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$
10.	$\text{NO}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{NO}_2$
11.	$\text{NO}_2 + \text{O} \rightarrow \text{NO}_3$
12.	$\text{NO}_3 \rightarrow \text{NO} + \text{O}_2$
13.	$\text{NO}_3 + \text{O} \rightarrow \text{O}_2 + \text{NO}_2$
14.	$\text{NO}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$
15.	$\text{N}_2\text{O}_4 \rightarrow \text{NO}_2 + \text{NO}_2$
16.	$\text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5$
17.	$\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$
18.	$\text{O}_2 + \text{O} \rightarrow \text{O}_3$
19.	$\text{O}_3 \rightarrow \text{O}_2 + \text{O}$
20.	$\text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2$
21.	$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$

The N pileup near the interface for the NO-annealed preoxides implies that the dominant transport during NO oxynitridation is NO molecular diffusion to the interface. To verify this idea with isotopic labeling, in **Figure 10** we present results of the reaction of an Si¹⁸O₂ film, oxidized initially with ¹⁸O₂, that is further reacted with N¹⁶O. It is evident that the N and ¹⁶O yields near the SiO_xN_y/Si interface overlap (centered at 4 nm below the surface). The classic Deal–Grove model [131] of silicon oxidation argues that SiO₂ film growth occurs by neutral molecular oxygen diffusing through the SiO₂ film and reacting at the SiO₂/Si interface. We [75, 111, 116, 117] and others [132–134] have refined the model, pointing out the existence of rather complex surface and near-interface (SiO₂/Si) reactions; however, the basic tenet of molecular O₂ diffusion still holds (at least for films >1.5 nm). No equivalent “standard” model for N incorporation during oxynitride growth exists. Two likely candidates to explain N incorporation are 1) direct N atom addition at the surface (from N₂O, NO, or N atoms present in the gas phase), and 2) NO diffusion to and reaction in the near-interfacial region, analogous to O₂ in the Deal–Grove model. If N or O atoms were present at the outer surface and diffused from the surface to the near-interface region, it is unlikely that both would pass atomically through the film without exchanging with lattice oxygen. The energy of an isolated, noninteracting interstitial N or O atom is very high and can be immediately lowered by insertion into an Si–Si, Si–N, or even Si–O bond. Although O is relatively more stable than N in an oxynitride, both O and N atoms should bond immediately to the lattice when present as isolated species inside the film. Isolated N or O atoms introduced at the surface should prefer to incorporate mostly at the surface, with a long tail decaying into the film. Since both N (and an equivalent or greater amount of O) atoms incorporate into the films with similar depth distributions (Figure 10), we propose that NO diffuses molecularly into the SiO₂ lattice (analogous to O₂ in the Deal–Grove model [131]). We further argue that NO should dissociate when it encounters unoxidized or partially oxidized Si, just as in the O₂ case, which should not occur until the NO (or O₂) reaches the near-interfacial region.

• N₂O oxynitridation

Gas-phase N₂O decomposition at high temperatures

In contrast to NO, which is a relatively stable molecule, N₂O decomposes rapidly at high temperatures. As we show below, the decomposition is a rather complex process. Gas flow rate, temperature, partial pressure of N₂O in the oxidizing ambient, reactor type (RTP vs. furnace) and geometry, and impurity levels are parameters which significantly affect the kinetics and the final

distribution of products [60, 61, 89, 135]. N_2O also decomposes under UV radiation [136, 137]. The multiparameter nature of the decomposition process makes it difficult to control N_2O processing and directly compare results obtained from different laboratories. An additional complication is that N_2O decomposition is an exothermic reaction which may cause nonuniformities of the temperature profile in a reactor [61, 138, 139].

Since NO_x chemistry has been studied extensively for many years [140] because of its crucial role in combustion reactions and in air pollution, a substantial database of reaction rates and activation energies exists [141]. We used a simple gas-phase reaction model and made computer simulations and analytical studies of the decomposing N_2O system, and found it possible to simplify the published mechanisms [79] (for example, Hartig and Tobin [135] use 80 steps) and still obtain similar results, even without including the effects of heat generation and transfer [139] and contaminants (e.g., H_2O) [135]. What we found is that of the many possible NO_x reactions known to occur (Table 2), the first five key steps seem to dominate the $N_2O \rightarrow NO$ decomposition. The rate-limiting one is the first step, $N_2O \rightarrow N_2 + O$. The N_2O decomposition obeys first-order kinetics. The initial rate law for N_2O decomposition is $R_0 = 2k_1[N_2O]$, but rapidly changes to $R = k_1[N_2O]$ as the reaction proceeds (k_1 is the reaction constant of the first reaction). The apparent activation energy for the decomposition of N_2O is 2.5 eV/molecule (2.4×10^2 kJ/mol). The characteristic decay time of the N_2O concentration is of the order of ~ 20 s at 1000 K (decreasing with temperature). The oxygen atoms then react further by the two key reactions $N_2O + O \rightarrow 2NO$ and $N_2O + O \rightarrow N_2 + O_2$. The branching ratio for these two reactions lies between 0.1 and 0.5 and varies with conditions. The rate law for NO formation is $R = k_1[N_2O]$, and the apparent activation energy for the formation of NO is 2.4 eV/molecule (2.3×10^2 kJ/mol).

As seen from Figure 11, the final concentrations of N_2 , O_2 , and NO obtained using 5-step and 21-step mechanisms over a temperature range of 1000 K–1400 K are as follows:

N_2 : 65.3%–59.3%, O_2 : 32.0%–25.7%, NO : 2.7%–15.0%;
(5 steps)

N_2 : 65.5%–59.9%, O_2 : 32.2%–26.5%, NO : 2.3%–13.6%.
(21 steps)

Data published by Hartig and Tobin [135] (using a much more complex mechanism) report the gas composition of decomposed N_2O at 1223 K as follows:

N_2 : 62%, O_2 : 28%, NO : 9.5%.

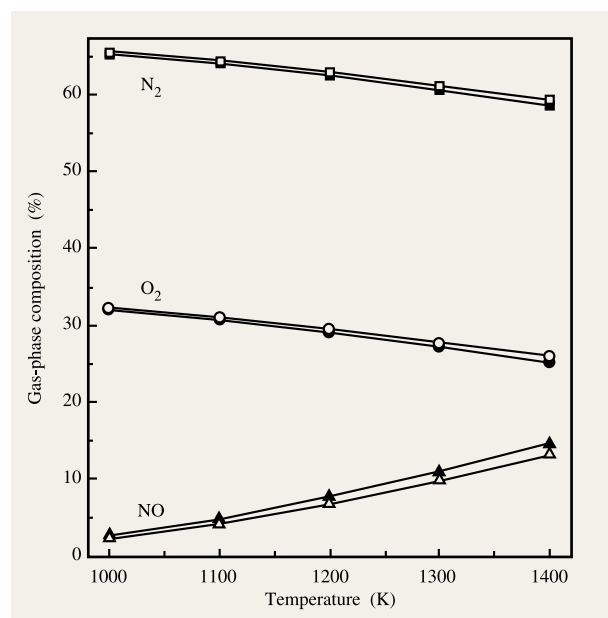


Figure 11

Steady-state composition of the main products (N_2 , O_2 , and NO) of gas-phase decomposition of N_2O , calculated in the scheme discussed in the text (solid symbols – 5 reactions; open symbols – 21 reactions).

This may be compared to N_2 : 64.3%, O_2 : 31.0%, and NO : 4.7% reported by Tobin et al. [89], who extracted the data from the early work of Briner et al. [140]. Finally, we note that the results of the calculations (Figure 11) agree qualitatively with recent mass-spectrometry observations of the gas-phase composition during N_2O decomposition in a furnace at 1223 K, viz., 61% N_2 , 27% O_2 , and 13% NO [142].

The main products of the N_2O decomposition are N_2 , O_2 , NO (with the equilibrium concentration of NO increasing with temperature). Since N_2 is much less reactive than O_2 and NO , one could expect that a properly chosen mixture of NO and O_2 in the gas phase would produce an oxynitride film similar to that grown in N_2O . However, this is not the case. We observed that oxynitridation in a mixture of NO and O_2 (with the variable fraction of NO at 20%, 40%, 60%) is in fact much more similar to NO oxynitridation than to N_2O oxynitridation [143]. This suggests that there are other active species present during N_2O decomposition which are important in the nitridation process. We believe [62], as do others [60, 61], that atomic oxygen plays a key role in N_2O oxynitridation (see the subsection which follows). Though the equilibrium concentration of O is rather low, an intermediate concentration of atomic oxygen released

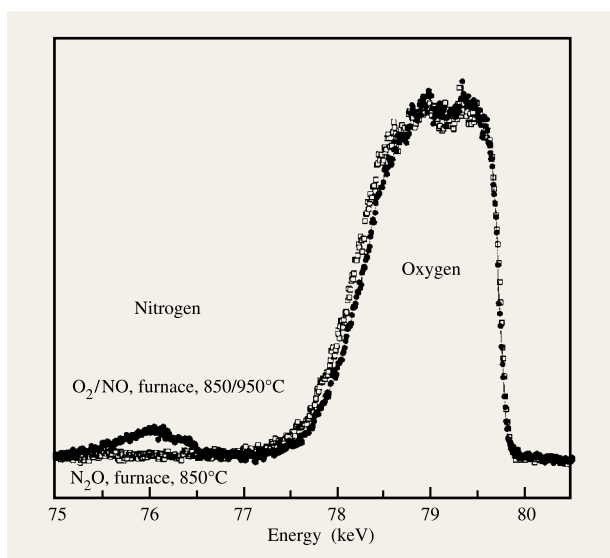


Figure 12

MEIS nitrogen and oxygen spectra for the films grown in N_2O (open symbols) and O_2/NO (solid symbols). Film thickness is ~ 5.5 nm. The O_2/NO film has about 1.6 ML (1 ML = $6.8 \times 10^{14} \text{ cm}^{-2}$) of nitrogen located within ~ 1.5 nm near the interface. The concentration of N in the N_2O -grown film is estimated to be less than 0.5 ML but is more broadly distributed in the film (after [74]).

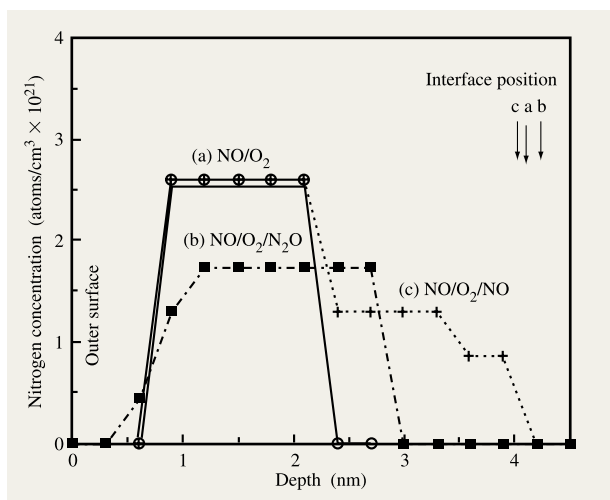


Figure 13

MEIS nitrogen depth profiles for an SiO_2 film (a) annealed in NO ; (b) subsequently annealed at 850°C in N_2O ; or (c) annealed in NO .

takes place near the wafer. Second, since oxygen radicals are very reactive, even a small partial pressure of atomic oxygen may have a significant effect on oxynitridation. Nitrous oxide (N_2O) has even been used in the surface science community to study the interaction of atomic oxygen with Si surfaces [144]. Finally, we note that reactions of N_2O with the Si wafer and the walls of the reactor may accelerate the decomposition process.

Nitrogen incorporation and removal during N_2O oxynitridation

Under equivalent conditions, N_2O yields less nitrogen incorporation than NO . **Figure 12** shows MEIS spectra for thin (~ 5 nm) oxynitride films grown in NO and N_2O under similar conditions. By integrating the areas under the nitrogen peaks of the spectra, one can readily see that the N_2O -grown oxynitride has much less incorporated nitrogen. The total concentration of nitrogen increases with temperature (Figure 4) and film thickness [20]. This implies that, in addition to thermal budget considerations, N_2O processing may not be an efficient source of nitrogen for films thinner than ~ 3 nm. The nitrogen distribution in the films is sensitive not only to the processing conditions but also to the reactor type [60, 61, 127]. Specifically, SiO_xN_y films grown in a furnace and in an RTP reactor have qualitatively different nitrogen depth profiles (Figure 3). The RTN_2O film shows N pileup near the interface, while the distribution of N in the furnace-grown film is broader. The difference was attributed to the gas-phase chemistry of N_2O decomposition (see the related subsection) and its subsequent effect on film composition. In the RTN_2O case, the decomposition takes place near the hot wafer [60, 84], so that most of the decomposition products (including atomic oxygen) can reach the wafer, whereas in a conventional furnace the gas decomposes in the hot inlet of the furnace before it reaches the wafer. This also explains gas-flow effects, i.e., lower nitrogen incorporation rates for lower N_2O flow rates.

The rate of film growth in N_2O is much slower than that in O_2 and is related to the amount of nitrogen in the film [20, 32, 142, 145]. Furthermore, the growth rate on the Si(100) surface is slower than that on the (111) and (110) surfaces [146]. Several attempts have been made to model the growth kinetics [82, 88, 142]. A model by Dimitrijevic et al. explains the slower growth rate by an exponential (with time) decrease of so-called “reactive sites” near the interface [82]. Other models used a scheme similar to the Deal–Grove model of the thermal oxidation of silicon [88].

The fundamental difference between oxynitridation in N_2O and NO is that while both incorporate nitrogen (by NO reactions near the interface), in the N_2O case the nitrogen incorporation occurs simultaneously with nitrogen removal from the upper layers of the film. Saks et al. found in $N_2O/O_2/N_2O$ studies that the final exposure of

in the first step of the decomposition process (Table 2) may be relatively high, especially if N_2O decomposition

the $\text{N}_2\text{O}/\text{O}_2$ -grown film (with nitrogen in the middle of the film) to N_2O results in nitrogen removal from the “bulk” of the film and new nitrogen incorporation near the interface [128]. Similar behavior was also observed in our MEIS studies (**Figure 13**). One can see that for an (NO/O_2) oxynitride film exposed to N_2O (i.e., $\text{NO}/\text{O}_2/\text{N}_2\text{O}$), the nitrogen concentration in the middle of the film decreases, whereas for the film annealed in NO (i.e., $\text{NO}/\text{O}_2/\text{NO}$) this effect was not observed—only incorporation of new nitrogen near the interface takes place. In these studies, the removal was also implied by an acceleration of the film growth.

There have been at least two alternative viewpoints on the mechanism of N removal: Carr et al. [60, 61] proposed that atomic oxygen causes nitrogen removal, whereas Saks et al. [128] argued that NO is responsible. Both NO and O are (intermediate) products of N_2O gas-phase decomposition at high temperatures (see the related subsection). Our recent $\text{NO}/\text{O}_2/\text{NO}$ experiments suggest that NO does not effectively remove nitrogen from the oxynitride. On the basis of this observation and the even distribution of nitrogen throughout NO-grown films (except for the topmost layer of the oxide) observed in our work (Figure 8) and by others [37], one can conclude that NO (when directly introduced as a key reactant) has a very low reactivity toward nitrogen removal compared to N_2O and its decomposition products [60, 128]. Exposure of an oxynitride film to ozone (an effective source of atomic oxygen) causes nitrogen removal from the film, which supports the atomic oxygen hypothesis [60]. However, the role of atomic oxygen in nitrogen removal must be better understood. We note that nitrogen is also removed from the film by a high boron flux from the polysilicon gate [147].

- *Mechanisms of nitridation in NO and N_2O and nitrogen profiles in the film*

Figure 14 is a schematic summary of the processes discussed above that occur during silicon (oxy)nitridation. N_2O rapidly decomposes in the gas phase to N_2 and O, and the O then initiates a further series of reactions to form NO, the key oxynitriding agent, and other species. NO is similar to O_2 when it interacts with Si and SiO_2 , in that the dominant oxynitride growth mechanism involves NO diffusion through an SiO_xN_y overlayer, followed by a reaction with silicon at and near the $\text{SiO}_x\text{N}_y/\text{Si}$ interface. The thermochemistry of the system is such that nitrogen, although thermodynamically unstable in the growing film relative to oxygen, appears to become kinetically trapped at the SiO_2/Si interface during growth. Alternatively, it may lower the interfacial stress, and therefore be stable only near the interface. The final nitrogen concentration and distribution is influenced by a competition between N incorporation and removal. The removal reaction is likely

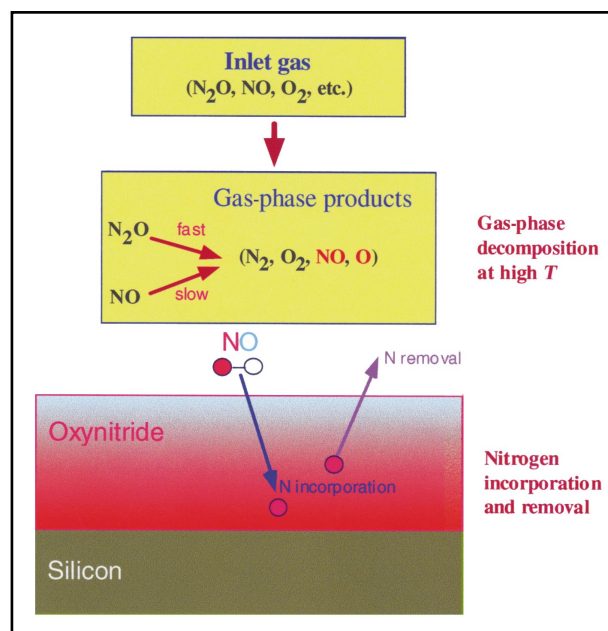


Figure 14

Schematic model of silicon oxynitridation in NO or N_2O .

due to atomic oxygen. Since the reactivities of NO, N_2O , and O_2 with Si, SiO_2 , and SiO_xN_y are quite different, properly chosen sequences of thermal reactions with Si can lead to oxynitride films with different nitrogen concentrations and profiles, and therefore electrical properties.

As an illustration, in **Figure 15** we schematically present several reaction sequences and resultant N profiles that we (and others) have observed. We note that most of the reactions are very condition-dependent; as pressure, film thickness, heating mode (conventional furnace vs. rapid thermal), etc. are changed, the N profiles can change significantly.

- *Nitridation in N_2*

Though molecular nitrogen is believed to be relatively inert, it was observed in early papers that annealing of SiO_2 films in N_2 results in the initial reduction of fixed oxide charge [98]. This behavior was attributed to the formation of an SiO_xN_y layer near the interface as monitored by XPS [87]. These nitridation reactions were performed in a furnace at high temperature ($>925^\circ\text{C}$) for ≥ 1 hr (i.e., requiring a high thermal budget). To reduce the thermal budget, we grew oxynitrides in nominally pure N_2 by rapid thermal processing [80]. We use the term “nominally” to mean that although the input N_2 gas stream is purified at the point of use and therefore extremely free of contaminants (less than 1 ppb each

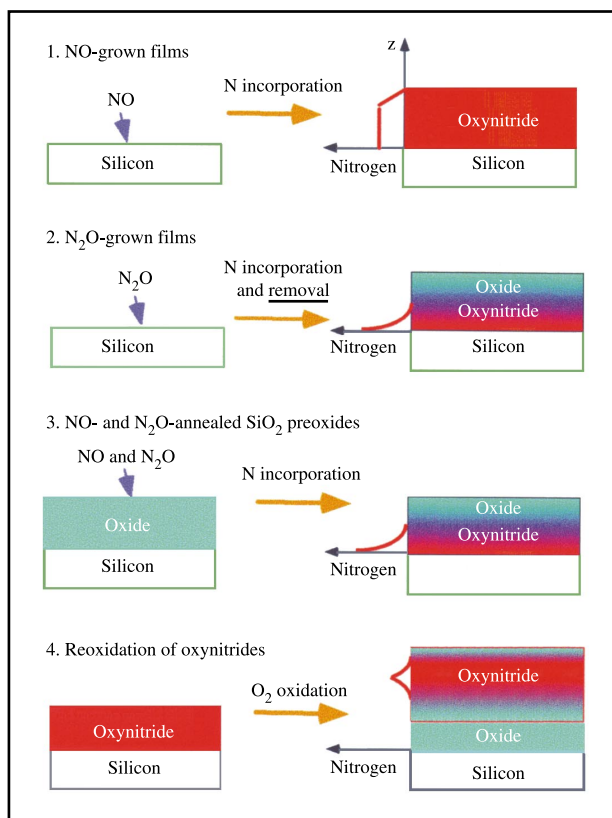


Figure 15

Nitrogen depth distributions for different nitridation sequences.

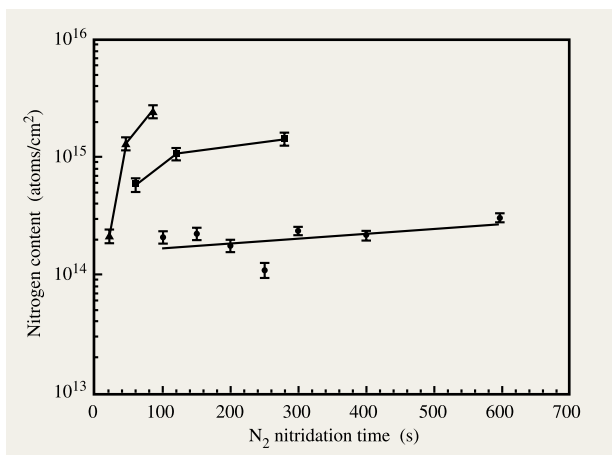


Figure 16

Kinetics of nitrogen accumulation during RTN₂ processing at 850°C (circles), 950°C (squares), and 1050°C (triangles) (after [80]).

of H₂O, O₂, CO₂, and CO), a cold-wall RTP module contributes impurities to the ambient through outgassing from the walls. Although the Si/N₂ system may be relatively inert for $T < 1200^{\circ}\text{C}$, the Si/N₂/H₂O/H₂/O₂ system is probably not. Thus, we observed that N₂ reacts with Si at moderate temperatures (850–1050°C) in an RTP module (due to the presence of gas-phase impurities) to form ultrathin (less than 1.2 nm) films as measured by ellipsometry (using $n = 1.47$), cross-sectional TEM, and MEIS.

Figure 16 illustrates nitrogen content (measured by NRA) as a function of N₂ nitridation time for RTN₂ treatment at various temperatures [80]. At 850°C, the nitrogen content is almost constant with time, whereas at the higher temperatures it increases and then may saturate with time. It can be seen from Figure 16 that anywhere from 0.2 to 3 ML of nitrogen can be incorporated, depending upon temperature and time. **Figure 17** is a plot of the ratio $N/(N + O)$ as a function of RTN₂ time at 850, 950, and 1050°C. The ratio increases with increasing temperature and time, and appears to approach that of the high-temperature stoichiometric compound Si₂N₂O. The RTN₂ films may consist of amorphous mixtures of SiO₂ and Si₂N₂O. Mixtures of Si₂N₂O, Si₃N₄, and SiO₂ phases have similarly been observed in plasma-deposited oxynitrides [148]. Oxygen and nitrogen depth profiling by MEIS shows a fairly uniform distribution of the elements in the films.

• Nitridation in NH₃

Nitridation in ammonia was one of the first methods used to incorporate relatively high (~10–15 at.%) concentrations of nitrogen into SiO₂ films [3, 10, 11, 59, 96]. XPS and AES depth profiles show that nitrogen piles up both at the interface and at the outer surface during the initial stages of nitridation [149]. The nitrogen-containing region near the interface was reported to be about 3 nm wide. As nitridation time increases, the concentration of nitrogen slowly increases, and the distribution becomes more uniform throughout the film [10, 11]. The thickness of the film remains essentially unchanged during nitridation. Nitrogen incorporation is enhanced by decreasing the SiO₂ film thickness [10, 11].

The nitridation atmosphere of NH₃ introduces high concentrations of hydrogen into SiO₂ films, which then can act as traps. SIMS analysis shows that the hydrogen concentration increases monotonically with nitridation time and becomes higher for higher temperatures. The hydrogen tends to pile up near the interface [150]. It has been shown that the high concentration of hydrogen can be reduced by a postnitridation anneal in a hydrogen-free ambient (e.g., N₂). It has also been found that the rate of hydrogen reduction is not dependent on the annealing gas (N₂ or O₂), indicating thermally activated out-diffusion

of hydrogen from the film [10, 11]. Because of the detrimental effects of hydrogen on device performance, lighter nitridation (lower temperature, shorter time) is desirable, since it introduces less hydrogen into the film.

Finally, we note that ammonia can be used for direct nitridation of Si. In this reaction scheme, NH_3 reacts with the Si surface at high temperatures to produce an ultrathin layer of silicon nitride [151–153], although again caution must be taken to minimize oxygen incorporation if it is not desired.

6. Nitridation by chemical and physical deposition methods

In this section, we briefly outline some deposition techniques for preparing ultrathin (oxy)nitride films. More details about deposition techniques can be found in review papers [19, 40]. CVD methods, using the existing “infrastructure” of commercially available reactors and precursors, are employed in many different silicon processing steps. High-temperature ($\sim 800^\circ\text{C}$) deposition of oxynitrides can be performed by reacting SiH_4 (or SiH_2Cl_2) with a mixture of N_2O and NH_3 . Without ammonia in the gas phase, no nitrogen incorporation takes place; only SiO_2 is deposited. The composition of the film, stress, refractive index, and growth rate are dependent on the flow rate. The concentration of incorporated nitrogen (and hydrogen) increases with an increase in the ratio of $\text{NH}_3/\text{N}_2\text{O}$ flow rate. The viability of this technique has been demonstrated for making device-quality ultrathin ($\sim 3\text{--}4\text{ nm}$) nitrided SiO_2 films and oxide/nitride stacks [18]. For this, reduced pressures of the reactants and RTP reactors are used. As with most other deposition methods, CVD requires postdeposition treatment to stabilize the film structure, drive hydrogen out, and minimize electrical defects. **Figure 18** shows nitrogen MEIS depth profiles for a 4-nm-thick RTCVD-deposited film (800°C , 3 Torr, N_2O flow rate of 500 sccm, $\text{NH}_3/\text{N}_2\text{O}$ ratio of 0.05, and $\text{SiH}_4/\text{N}_2\text{O}$ ratio of 0.0128) after annealing in Ar, O_2 , and N_2O . One can see that the film annealed in Ar has nitrogen distributed almost evenly in the film, while annealing in N_2O causes nitrogen removal from the film, as discussed in the subsection on nitrogen incorporation and removal during N_2O oxynitridation. Finally, we note the interesting idea of oxynitride deposition at quite low temperature (330°C) using photo-enhanced CVD of Si_2H_6 , NH_3 , and NO_2 [154].

Plasma-assisted nitridation is a well-known deposition method for low-temperature processing [19, 40, 49, 155]. First discussed in the 1970s, several reaction schemes and different reactor types (e.g., rf, ECR, etc.) have been reported for plasma-enhanced deposition of silicon nitride. The traditional scheme includes the reaction of SiH_4 and NH_3 in a plasma at $200\text{--}400^\circ\text{C}$. The use of N_2 instead of ammonia helps to reduce the hydrogen content in the film;

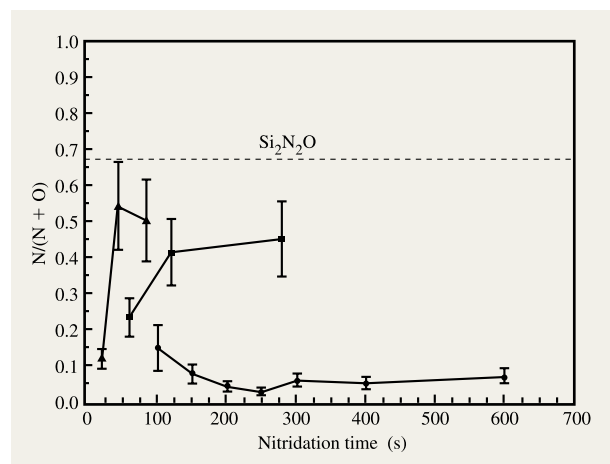


Figure 17

Ratio of $\text{N}/(\text{N} + \text{O})$ in ultrathin films grown by RTN_2 processing at 850°C (circles), 950°C (squares), and 1050°C (triangles). The dashed line shows the ratio for the $\text{Si}_2\text{N}_2\text{O}$ oxynitride phase (after [29, 80]).

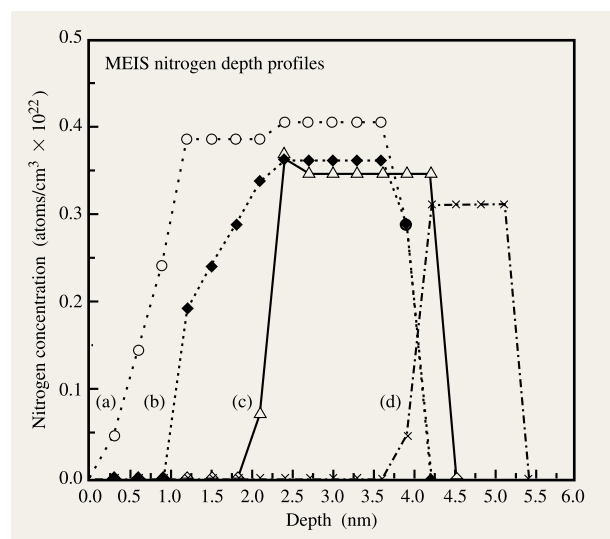


Figure 18

MEIS nitrogen depth profiles for an oxynitride film grown by an RTCVD method annealed in (a) Ar at 800°C for 30 s; (b) O_2 at 1000°C for 30 s; (c) N_2O at 900°C for 15 s; and (d) N_2O at 1000°C for 30 s. The samples were made by E. Vogel and J. J. Wortman (NCSU).

however, ionization of nitrogen is more difficult. N_2O can also be used for plasma-assisted nitridation of ultrathin SiO_2 films. To minimize the damage to the substrate by

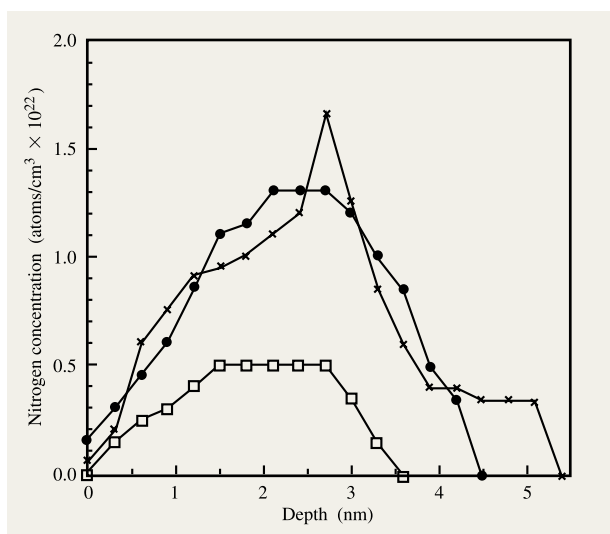


Figure 19

MEIS nitrogen depth profiles for an ~3.5-nm SiO₂ film implanted with nitrogen ions with an energy of 200 eV (squares), 500 eV (solid circles), and 1000 eV (crosses). The implantation dose is 10¹⁶ ions/cm².

energetic particles, a remote plasma deposition method has been developed [19]. In this process, the nitrogen-containing species are plasma-excited outside the reactor chamber. Then the excited species are extracted from the plasma region and react with the substrate. As in the case of the conventional CVD process, the composition of the film is determined in part by the ratio of gas flow of the reactive species. More details about plasma-assisted nitridation can be found in review papers [19].

Another nitridation technique based on energetic nitrogen particles is low-energy ion implantation [45–47, 50–52, 55, 84, 156]. The nitridation of the gate-oxide film can be performed in two different sequences: low-energy nitrogen ions can be implanted into already grown oxide, or nitrogen can be implanted into the silicon substrate, which is subsequently oxidized [83, 84, 156]. In the former case, the energy of the nitrogen ions should be low enough to avoid penetration (and damage) to the silicon substrate. The penetration depth of the ions decreases with ion energy. As a reference, the penetration depth of 1-keV nitrogen ions in SiO₂ is about 4 nm and decreases to ~2.3 nm for 0.5-keV ions, which sets a limit for the ion energies for ultrathin oxides. **Figure 19** shows MEIS nitrogen depth distributions for an ~3.5-nm SiO₂ film nitrided by implantation of nitrogen ions of different energies. These data illustrate the increasing penetration depth and concentration of incorporated nitrogen (for the same dose) with ion energy. The mechanism of low-energy

implantation is different from that of conventional high-energy implantation [55]. When the low-energy ion approaches the surface, it becomes neutralized within about 1 nm of the surface. As a result, the nitridation is then caused by diffusion, reaction, and desorption of this hot nitrogen atom. Owing to desorption (and sputtering) steps, this complex process typically results in a concentration of implanted nitrogen that is lower than the implantation dose. When the nitrogen ions are implanted into the silicon prior to the oxidation, a reduction in reliability is observed [156]. Subsequent high-temperature oxidation results in the loss of some nitrogen, and its segregation and accumulation near the interface, which in turn leads to improved electrical properties.

The recently developed jet vapor deposition (JVD) method utilizes a high-speed jet of a light carrier gas to transport the relevant species onto the Si substrate to form nitride films at room temperature [43]. In this process, diluted silane and a mixture of N₂ + He flow through nozzles into a microwave discharge region near the outer nozzle exit. Reactive Si species and N atoms formed in the discharge region are transported in the sonic He jet to the Si substrate, where they form a nitride. The film composition and growth rate are determined by the SiH₄/He/N₂ ratio and the flow rate. This technique has been shown to be capable of producing device-quality (both capacitors and transistors) ultrathin films. However, the uniformity of ultrathin films deposited over a large wafer (limited by the small size of the nozzle) and oxygen incorporated into the film are of concern for practical applications.

Atomic layer deposition, or ALD (also known as atomic layer epitaxy, ALE, or atomic layer CVD, AL-CVD), a technique based on selective reactivity of gaseous and surface species, allows one to produce in a controlled manner ultrathin films with a rate of approximately one monolayer per deposition cycle [157, 158]. This technique has been used to deposit thin films of various dielectric materials, including SiO₂. However, to the best of our knowledge, a procedure for preparing nitrided SiO₂ films by ALD has not yet been established. Goto et al. proposed a process of making thin (2–10 nm) silicon nitride films by repetitive plasma nitridation cycles of Si by NH₃ and deposition of Si by SiH₂Cl₂ thermal reaction [44]. The deposition rate was found to be nearly half a monolayer per deposition cycle, and the deposited films showed thickness uniformity much better than that of remote plasma CVD films [44].

Finally, we note that very reactive nitrogen atoms can be used for Si and SiO₂ nitridation, as was demonstrated in early studies [53, 54]. The interaction of nitrogen atoms with a silicon surface can produce a thin (~2–3 nm) layer of silicon nitride. However, the practical use of the nitrogen atoms in the near future may be limited by

the lack of available sources of atomic nitrogen that can generate a uniform beam over a large wafer.

7. Nitrogen engineering of ultrathin nitrided oxides

On the basis of our understanding of the kinetics and thermodynamics of nitrogen incorporation in SiO_2 , ultrathin oxynitride films with nitrogen-enhanced layers located in specific regions of a film can be achieved. Both thermal nitridation methods and deposition techniques can be used. To tailor the nitrogen content and distribution within the ultrathin dielectric by a thermal method, one can employ the fact that N_2O , NO , and O_2 gases behave differently with respect to nitrogen incorporation and removal, as discussed in the subsection on nitrogen incorporation and removal during N_2O oxynitridation.

One thermal process scheme that we have used to achieve a double-peaked nitrogen profile is as follows [81]. First, a thin oxide layer containing a high concentration of nitrogen is grown by reacting NO with Si . (Other surface nitridation methods may also work, though some of the techniques, for example N_2O oxynitridation, may yield an insufficient concentration of nitrogen in ultrathin films [33].) The oxynitride film is then reoxidized in O_2 , which results in a new oxide layer grown beneath the original oxynitride. We and others have demonstrated that such reoxidation does not significantly change the already incorporated nitrogen concentration [62, 128]. In the third step, the sample is nitrided in NO —a key step. NO diffuses to the interface and does not remove nitrogen from the interior of the film [62, 76]. Therefore, the top nitrogen peak remains undisturbed. The MEIS results (**Figure 20**) clearly demonstrate that the $\text{NO}/\text{O}_2/\text{NO}$ sample has nitrogen-enhanced layers located near both the top ($\text{SiO}_2/\text{polysilicon}$) and bottom (Si/SiO_2) of the oxynitride film. One can see that a longer third-step NO annealing time (40 min) results in a higher concentration of nitrogen near the interface. In this scheme, one should be careful using N_2O in the final step, because it removes incorporated nitrogen. Finally, we note that nitrogen-layered structures can also be produced by deposition methods [18, 19, 41, 49]) or by a combination of thermal nitridation/deposition methods.

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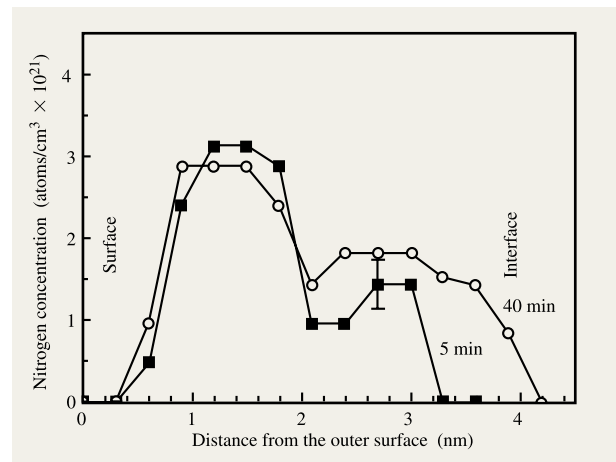


Figure 20

Nitrogen double-layered structure produced by an $\text{NO}/\text{O}_2/\text{NO}$ processing for two different times of the final NO anneal: 5 min (squares) and 40 min (circles) (after [81]).

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